

EYDUS, Ya. T.

*Chem* Catalytic hydrocondensation of carbon monoxide with olefins. XVII. Participation of 2-butene in hydrocondensation reaction with carbon monoxide. Ya. T. Efdus and R. I. Izmailov (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1936, 809-72; cf. *C.A.* 51, 1813c.—Examm. of previous exptl. data indicate that hydrocondensation of CO with 1- or 2-butenes yields aliphatic hydrocarbons of normal structure with little branching. Apparently 2-butene isomerizes to 1-butene to a large extent before entering the reaction. The product from 1-butene is more unsatd. and of lower mol. wt. than that formed from 2-butene.

G. M. Kosolapoff

*AM*

7  
Verification, by means of labeled alcohol, of the dehydration-condensation mechanism of formation of the hydrocarbon chain in synthesis of hydrocarbons from carbon monoxide and hydrogen. O. A. Golovina, S. Z. Kozlovskii, M. M. Sakharov, and Ya. I. Eklus. *Dokl. Akad. Nauk S.S.S.R., Sect. Chem.* 198, 1459 (1969) (English translation).—See C.A. 50, 14591d.

Chem

PM

*Y. DUS, YA. T.*

USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 2, 1958, 3897.

Author : O.A. Golovina, S.Z. Roginskiy, M.M. Sakharov, Ya. T. Eydus.

Inst : Academy of Sciences of USSR.

Title : Checking Dehydration-Condensation Mechanism of Hydrocarbon Chain Formation at Hydrocarbon Synthesis of CO and H<sub>2</sub> by Tagged Alcohol.

Orig Pub: Dokl. AN SSSR, 1956, 108, No 2, 253-255.

Abstract: Hydrocarbon (HC) synthesis of CO and H<sub>2</sub> was carried out on Co catalyst at 195° with the addition of C<sub>2</sub>H<sub>5</sub>OH tagged with C<sup>14</sup> to the initial gas mixture. The drop of specific radioactivity (SR) with the increase of their molecule length and the stability of the molecular radioactivity SR in molecules containing over 5 C atoms was established. The revealed molecular radioactivity SR stability indicates a chain mechanism

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USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimii, No 2, 1958, 3897.

of the hydrocarbon molecule growth on the catalyst surface with the participation of alcohol in the initiation or breaking of flat growing chains. At the same time the authors are of the opinion that the data obtained by them, as well as the data of Kammer and Emmett (RZhKhim, 1954, 49641) are not enough to disprove the methylene scheme and to support the dehydration-condensation synthesis scheme promoted by Storch, Golambik and Anderson (Sintez uglevodorodov iz okisi ugleroda i vodoroda, Izd-vo inostr. literatury, M., 1954, 499).

Card : 2/2

-24-

GOLOVINA, O. A., ROGINSKIY, S. Z., SAKHAROV, M. M., EYDUS, Ya. T., DOKUKINA, Ye. S.

"Study of the Role of Plane Chains in the Synthesis of Hydrocarbons from CO and H<sub>2</sub>"

Problems Kinetics and Catalysis, v. 9, Isotopes in Catalysis, Moscow, Izd-vo AN SSSR, 1957, 442p.

Most of the papers in this collection were presented at the Conf on Isotopes in Catalysis which took place in Moscow, Mar 31- Apr 5, 1956.

*EYDUS Ya. T.*  
GOLOVINA, O.A.; ROGINSKIY, S.Z.; SAKHAROV, M.M.; EYDUS, Ya.T.; DOKUKINA, Ya.S.

Function of straight chains in the synthesis of hydrocarbons from  
CO and H<sub>2</sub>. Probl. kin. i kat. 9:76-83 '57. (MIRA 11:3)  
(Hydrocarbons) (Carbon--Isotopes)

*Eydus, Ya. T.*  
AUTHORS: Eydus, Ya. T., Ordjan, M. B.

62-11-25/29

TITLE: On Catalytic Hydrocondensation of Carbon Monoxide With Olefines.  
(O kataliticheskoy gidrokondensatsii okisi ugleroda s olefinami).  
18.Report. Hydrocondensation of the Carbon Monoxide With Penten-1  
and Isomerization of the Latter Into Pentene-2 Under Conditions of  
This Reaction (Soobshcheniye 18. Gidrokondensatsiya okisi ugleroda  
s pentenom-1 i izomerizatsiya poslednego v penten-2 v usloviyakh  
etoy reaktsii)

PERIODICAL: Izvestiya AN SSSR, Otdel. Khim. Nauk, 1957, Nr 11, pp. 1408-1410  
(USSR)

ABSTRACT: It is shown that under presence of  $H_2$  and Co the pentene-1 enters  
into hydropolymerization- and hydrocondensation-reaction with CO  
with 28-30% at  $190^\circ$ , that it is isomerized into pentene-2 with  
28-30%, hydrogenized into pentane with 25-27% and suffers a hydro-  
cracking with 3%. The hydrocondensate after the hydrogenation is  
a mixture of limit hydrocarbons of normal structure, with an un-  
important admixture of slightly ramified ones. There are 1 figure,  
4 tables, and 8 references, 7 of which are Slavic.

ASSOCIATION: Institute for Organic Chemistry imeni N. D. Zelinskiy of the AN  
USSR (Institut organicheskoy khimii im. N. D. Zelinskogo Akademii  
nauk SSSR)

Card 1/2

On ~~Catalytic~~ Hydrocondensation of Carbon Monoxide With Olefines. 62-11-25/29  
18.Report. Hydrocondensation of the Carbon Monoxide With Penten-1 and Iso-  
merization of the Latter Into Pentene-2 Under Conditions of this Reaction.

SUBMITTED: July 1, 1957

AVAILABLE: Library of Congress

Card 2/2



Eydus, Ya. T.

AUTHORS: Eydus, YA. T. and Izmaylov, R. I. (Moscow)

TITLE: Reaction of Isomerization in a Series of Butenes (Reaktsii izomerizatsii v ryadu butenov).

PERIODICAL: Uspekhi Khimii, 1957, Vol. 26, No. 2, pp. 212-238, (U. S. S. R.)

ABSTRACT: Extensively referenced article containing much tabular data. The author's main points can be summarized as follows: Molecules of butenes are the simplest systems inclined to reactions of isomerization and the following classifications can be distinguished: 1) a displacement of the double bond (olefinic link) in butenes of normal structure, with a conversion of butene-1 to butene-2, and vice versa; 2) cis-trans-isomerization of butene-2 and 3) skeletal isomerization with a conversion of n-butenes to isobutene and vice versa. The theoretically conceivable isomerization of butenes by way of cyclization to cyclobutane or methyl cyclopentane has not yet been realized. The reactions indicated, in addition to their theoretical interest, have a practical significance in the production of isooctane, synthetic rubber, and lubricating oils, since not all isomer butenes are equally suited as initial products in the production of various

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# Reaction of Isomerization in a Series of Butenes

Table 1 gives data on content in % of butene-2 (cis- and trans-form) in an equilibrium mixture of n-butenes ( $t^{\circ}$  from 200-500 $^{\circ}$ ). Table 2 presents data on the content of n-butenes in an equilibrium mixture ( $t^{\circ}$  from 27-727 $^{\circ}$ ), wherein a comparison is made of the composition of equilibrium mixtures of n-butenes computed by A. V. Frost (8) with corresponding data obtained experimentally by other authors (H. H. Voge, N. C. May [4]). Table 3 gives data on the free energies and equilibrium constants of the isomerization of butenes (in an ideal gaseous state) ( $t^{\circ}$  from 25 to 1227 $^{\circ}$  C.). Table 4 presents values of equilibrium concentrations of butenes (in an ideal gaseous state,  $t^{\circ}$  from 25-1227 $^{\circ}$  C. for butene-1, butene-2, butene-2 [trans], and isobutene). Table 5: content of butene-1 and butene-2 in a mixture in dependence on volumetric velocity (velocity space).

The outstanding personalities cited in text are: F. E. Frey and W. F. Huppke, for their study on the dehydrogenization of n-butane at  $t^{\circ}$  of 350-500 $^{\circ}$  under conditions of the absence of isobutene in the

Card 3/4

ЕYDVS, ya. T.  
USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-  
chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 2, 1958, 3898.

Author: O. A. Golovina, Ye. S. Dokukina, S. Z. Roginskiy, M. M. Sakharov,  
Ya. T. Eyduz.

Inst: Academy of Sciences of USSR.

Title: Study of Flat Chain Part in Hydrocarbon Synthesis of CO and H<sub>2</sub>.

Orig Pub: Dokl. AN SSSR, 1957, 112, No 5, 864-867.

Abstract: Experiments of hydrocarbon synthesis of Co and H<sub>2</sub> were carried out at 195° on a catalyst of the composition 100 Co : 18 ThO<sub>2</sub> : 100 kieselguhr with addition of 0.88 or 1.45% by volume of C<sub>2</sub>H<sub>4</sub> (I) tagged with C<sup>14</sup> to the initial gas mixture of the composition 1CO - 2H<sub>2</sub>. It was established that the molar radioactivity (A) of the formed hydrocarbons was stable and did not depend on their molecular weight. The synthesis product yield did not practically change at the change of the tagged I concen-

-USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 2, 1958, 3898.

tration, but the ratio of A of the initial I to the mean A value of produced hydrocarbons, which is equal to 9.6 at 0.78% by volume of I in the initial gas mixture, drops to 4.5 at 1.45% by volume of I. The obtained results indicate the I participation in the initiating of flat growing chains on the catalyst and the close formation speeds of the initiating complex along two parallel ways: with the participation of the added I in the complex formation, and without it. The authors are of the opinion that the obtained results, as compared with the results of an earlier work of hydrocarbon synthesis of CO and H<sub>2</sub> with the addition of tagged C<sub>2</sub>H<sub>5</sub>OH (See the foregoing abstract) compel one to doubt the correctness of the dehydration-condensation mechanism proposed for the hydrocarbon synthesis on the Co catalyst.

*Ey Dus, YA. T.*  
AUTHORS:

Yershov, N. I., and Eydus, Ya. T.

20-5-20/48

TITLE:

The Experimental Verification of the Chain-Mechanism of the Hydro-  
polymerization of Olefines, a Heterogeneous-Catalytic Reaction Pro-  
ceeding Under the Influence of Carbon Dioxide and Hydrogen (Ekspe-  
rimental'noye obosnovaniye tsepnogo mekhanizma geterogenno-kataliti-  
cheskoy reaktsii gidropolimerizatsii olefinov, protekayushchey pod  
vliyaniyem oksii ugleroda i vodoroda).

PERIODICAL: Doklady AN SSSR, 1957, Vol. 115, Nr 6, pp. 1126-1128 (USSR.).

ABSTRACT:

The chain-reactions proceeding in space and being initiated by free  
atoms or by radicals are well known and have been thoroughly studied.  
But a direct and unequivocal experimental proof that this reaction  
may take place on the surface of a solid catalyst, is hitherto lacking.  
It was proved, indeed, that some reactions take place on solid cata-  
lysts according to the radical-mechanism, and a possibility of a  
heterogeneous-catalytic reaction was left open in theoretical works.  
The authors had earlier shown that the radicals forming in heteroge-  
neous-catalytic reductions of carbon-oxide by hydrogen are initiators  
of the hydropolymerization of olefines. It was interesting to deter-  
mine whether this reaction did not have a chain character. One of

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23-6-20/48

The Experimental Verification of the Chain-Mechanism of the Hydropolymerization of Olefines, a Heterogeneous-Catalytic Reaction Proceeding Under the Influence of Carbon Dioxide and Hydrogen.

the characteristic peculiarities of the homogeneous chain reactions of the polymerization of olefines, under the influence of free alkyl radicals, is the dependence of the chain length, or the yield in relation to the initiator, on the concentration of these radicals. It was observed that the yield in relation to the initiator increases with a decrease in the concentration of the free radicals. The heterogeneous-catalytic character of the reaction manifests itself in the influence exerted by the olefine adsorption on the reaction: The reaction only takes place when an adsorbed olefin exists on the catalyst. Carbon dioxide with its stronger inclination toward adsorption blocks up, e. g., the surface of the catalyst in the case of propylene. Thus the hydropolymerization reaction gets stuck at the surface due to the absence of propylene. From this follows that the hydropolymerization reaction of olefines under the influence of carbon oxide and hydrogen represents a heterogeneous-catalytic reaction with a chain mechanism. The possibility of a proceeding of heterogeneous-catalytic reactions according to the radical - chain - mechanism was for the first time verified here by the example of this reaction. It is quite probable that the formation of hydro-carbons from CO and H<sub>2</sub> in a

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The Experimental Verification of the Chain-Mechanism of the 20-6-20/48  
Hydropolymerization of Olefines, a Heterogeneous-Catalytic Reaction Proceeding  
Under the Influence of Carbon Dioxide and Hydrogen.

related hydropolymerization reaction in a certain stage also proceeds according to the chain-radical mechanism. The initial state takes place under olefine-formation according to the radical mechanism (hydrocondensation). The hydropolymerization begins with the accumulation of olefines on the surface of the catalyst. It is complicated by a number of other reactions (hydrocracking, hydration etc.) and now proceeds according to the chain mechanism. The formation of hydrocarbons takes place in more complicated combinations of the radical with the chain-radical-mechanism. The authors further became convinced of the common character of the hydropolymerization and of the formation of hydrocarbons from CO and H<sub>2</sub>

by the fact that their dependence on temperature is identical and the nature of their reaction products is very similar. There are 1 figure and 9 Slavic references.

ASSOCIATION: Institute for Organic Chemistry AN USSR im.N.D.Zelinskiy(Institut organicheskoy khimii im.N.D.Zelinskogo Akademii nauk SSSR.).

Card 3/4

The Experimental Verification of the Chain-Mechanism of the  
Hydropolymerization of Olefines, a Heterogenous-Catalytic Reaction Proceeding  
Under the Influence of Carbon Dioxide and Hydrogen. 20-6-20/48

PRESENTED: By B. A. Kazanskiy, Academician, April 19, 1957

SUBMITTED: April 19, 1957.

AVAILABLE: Library of Congress.

Card 4/4



AUTHORS: Eydus, Ya. T., and Ordyan. M. B.

20-1-27/44

TITLE: On the Methylation of Cyclopentenones by Methylene Radicals that Form When Carbon Monoxide is Reduced by Contact with Hydrogen  
(O metilirovanii tsiklopentena metilenovymi radikalami, obrazuyushchimisya kontaktnym vosstanovleniyem okisi ugleroda vodorodom).

PERIODICAL: Doklady AN SSSR, 1957, Vol. 116, Nr 1, pp. 101-104(USSR).

ABSTRACT: It was earlier proved that in the reaction of the catalytic hydrocondensation of carbon monoxide with olefines a methylation of cyclohexene by methylene radicals takes place which form due to a hydration of CO by contact with hydrogen. From this develop monomethyl- and 1,2-dimethyl substitutes of cyclohexene. It was earlier experimentally proved that in the catalytic synthesis of hydrocarbons from CO and H<sub>2</sub> by methylation of benzene in toluol an intermediate formation of methylene radicals takes place. In the present paper the results of the study are described which were obtained from the investigation of the behavior of another cyclo-olefine, of cyclopentene-toward the hydrocondensation reaction with carbon monoxide. The apparatus and the test arrangement remained the same as in earlier works. The production method and the properties of the initial cyclopentene

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On the Methylation of Cyclopentenones by Methylene Radicals 20-1-27/44  
that Form When Carbon Monoxide is Reduced by Contact with Hydrogen.

are described. Before the actual problem (see above) the behavior of the mentioned substance alone and in a mixture with hydrogen was studied. In the latter case the hydro-genation to cyclopentane (about ~50% calculated on cycloolefine) took place as the only reaction. Neither hydro-cracking nor hydrogenolysis of the 5-member cycle occurred. On the passage of cyclopentene through a gas mixture with Co and H<sub>2</sub> the liquid catalysate on the whole consisted of cyclopentene and cyclopentane-mixture. The fraction 43,6 - 44,2° contained small amounts of aliphatic hydrocarbons which had formed from CO and H<sub>2</sub>. On hydration of the liquid catalysate over platinized charcoal with addition of H<sub>2</sub>PtCl<sub>6</sub> reaction products which boiled higher than cyclopentane were contained in a quantity of 4 - 4,5%. The hydrogenisate was subjected to fractionzated distillation. Figure 1 shows the fractionation curve. It has 3 wide plateaus which correspond to fractions II, IV and V. The results of an optical analysis showed that fraction II consists of almost pure methyl-cyclopentane with traces of cyclohexane. Fraction III contained 60% of the former and 40% of the latter substance, fraction IV - 10% of the latter and 35% of the former. Fraction V contained considerable amounts of ethyl-cyclohexane, ethylcyclopentane and propylcyclopentane.

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On the Methylation of Cyclopentenes by Methylene Radicals that 20-1-27/44  
Form When Carbon Monoxide is Reduced by Contact with Hydrogen.

tane as well as small amounts of methyl-cyclohexane. In all fractions the presence of small amounts of paraffin-hydrocarbons is possible which may form from CO and H<sub>2</sub>. As far as in the reaction of cyclopentene with CO and H<sub>2</sub>, as shown above, no hydro-cracking of the cycloolefine or the cycloparaffin formed from it takes place, all hydrocarbons with a side-chain on the 5-member cycle, which can only have developed by isomerization of a 5-member hydrocarbon with a side-chain, formed thanks to the hydrocondensation of cyclopentene with CO. About 3% of the CO that entered the reaction was converted to CO<sub>2</sub>, ~53% - to aliphatic hydrocarbons according to the Orlov-Fischer-Tropsch reaction. The yield of the above-mentioned cyclic hydrocarbons amounted to ~33% of the initial CO and 44% of the CO that went through the reaction, when it is calculated that every carbon atom of the side-chains as well as a carbon atom of the 6-member cycle were transferred from the CO-molecule. Thus, due to the hydrocondensation of cyclopentene with CO in the presence of H<sub>2</sub>, a side-chain forms on the 5-member cycle. methyl-, ethyl- and propyl-

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On the Methylation of Cyclopentenes by Methylene Radicals that 20-1-27/44  
Form When Carbon Monoxide is Reduced by Contact with Hydrogen.

radicals. At the same time an expansion of the 5-member cycle takes place under formation of the corresponding hydrocarbons with a 6-member cycle and a side-chain from a methyl- or an ethyl-radical or without a side-chain. A large portion of the initial cyclopentene is reduced to cyclopentane. There are 1 figure, 1 table and 7 references, 6 of which are Slavic,

ASSOCIATION: Institute for Organic Chemistry AS USSR imeni N.D. Zelinskiy (Institut organicheskoy khimii imeni N. D. Zelinskogo Akademii nauk SSSR).

PRESENTED: By B. A. Kazanskiy, Academician, April 24, 1957.

SUBMITTED: April 23, 1957.

AVAILABLE: Library of Congress.

Card 4/4

AUTHORS: Eydus, Ya. T., Ordyan, M. B., 62-2-25/28

TITLE: On the Catalytic Hydrocondensation of Carbonmonoxide With Olefines (O kataliticheskoy gidrokondensatsii okisi ugleroda s olefinami) Information 19: The Hydrocondensation of Carbon Monoxide With Pentene-2. The Mutual Transformation of Pentene-2 and Pentene-1 on the Conditions of This Reaction (Soobshcheniye 19. Gidrokondensatsiya okisi ugleroda s pentenom-2. Vzaimnoye prevrashcheniye pentena-2 i pentena-1 v usloviyakh etoy reaktsii)

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 2, pp. 243-246 (USSR)

ABSTRACT: The investigation results concerning the behaviour of pentene-1 under the conditions of the hydrolytic hydrocondensation of carbon monoxide with olefines were reported earlier. The present paper reports on the performed investigation of the behavior of pentene-2. The latter was synthesized of  $C_2H_5Br$  and  $HCOOCH_3$  over the stages of pentanol-3, its acetate with a pyrolysis of it (boiling point  $36,3^{\circ}C$ , 760 mm torr). The catalyst, the apparatus and the order of experiments remained the

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On the Catalytic Hydrocondensation of Carbonmonoxide With Ole- 62-2-25/28  
fines. Information 19: The Hydrocondensation of Carbon Monoxide With Pentene-2.  
The Mutual Transformation of Pentene-2 and Pentene-1 on the Conditions of This  
Reaction .

same as in the investigations already reported. It was shown  
that in the presence of  $H_2$  and CO (at  $190^\circ$ ) a hydropolymeri-  
zation and hydrocondensation takes place on pentene-2 with CO  
(see tables 1-4). After hydrogenation the product of hydro-  
condensation represents a mixture of saturated hydrocarbons.  
This indicates that the hydrocondensation (pentene-2 with CO)  
is preceded by an isomerization to pentene-1. There are 4 tab-  
les, 7 references, 6 of which are Slavic.

ASSOCIATION: Institute for Organic Chemistry imeni N. D. Zelinskiy AN USSR  
(Institut organicheskoy khimii im. N. D. Zelinskogo Akademii  
nauk SSSR)

SUBMITTED: October 11, 1957

AVAILABLE: Library of Congress

Card 2/2 1. Pentene-2-Synthesis 2. Pentene-1<sup>2</sup>-2-Transformations  
3. Carbon monoxide-Condensation reactions 4. Olefines-  
Condensation reactions

SOV/20-120-2-27/63

AUTHORS: Eydnus, Ya. T., Puzitskiy, K. V., Ryabova, K. G.

TITLE: On the Synthesis of Esters and Other Derivatives of Carboxylic Acids From Carbon Monoxide, Olefines and Acetylating Compounds Under Conditions of Acid Catalysis (O sinteze slozhnykh efirov i drugikh proizvodnykh karbonovykh kislot v usloviyakh kislotochnogo kataliza iz okisi ugleroda, olefinov i atsiliruyushchikhsya soyedineniy)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 2, pp. 323 - 325 (USSR)

ABSTRACT: These reactions have been very little investigated. They were hitherto only performed in the simultaneous presence of all initial components in the reaction mixture and under very hard conditions. The yields were fairly small. In the present paper new ways of synthesis of these esters are described which lead to success under conditions very mild for such reactions: at 0 - 50°C and a pressure of from atmospheric absolute pressure to 80 atmospheres excess pressure. Possibilities of synthesis of other derivatives of carboxylic acids under analogous con-

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On the Synthesis of Esters and Other Derivatives of SOV/20-120-2-27/63  
Carboxylic Acids From Carbon Monoxide, Olefines and Acetylating Compounds  
Under Conditions of Acid Catalysis

ditions are also discussed. This synthesis was obtained in 2 stages. At first only olefines and CO were present in the reaction mixture which, due to interaction with the catalyst (concentrated sulfuric acid), formed an intermediate complex. Then alcohol was added which reacted with the complex and formed the desired esters,  $H_2SO_4$  being regenerated. The theoretical examination of the nature of this intermediate complex permits to draw the following conclusions: 1) The complex possesses properties of an acetylating agent. 2) The complex is according to its composition and structure very close, if not identical (Reference 4), to the mixed  $H_2SO_4$ -anhydride and the anhydride of carboxylic acid. 3) The formation of the complex takes place under the temporary formation of carbonium-ions. From these conclusions reaction schemes are set up. In the present paper the results obtained by the authors in the investigation of the formation reaction of methyl ester of carboxylic acids from isobutylene as well as from liquid olefines are shortly described.

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On the Synthesis of Esters and Other Derivatives of SOV/20-120-2-27/63  
Carboxylic Acids From Carbon Monoxide, Olefines and Acetylating Compounds  
Under Conditions of Acid Catalysis

Details are described in a kind of experimental part. There are 7 references, 1 of which is Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, AS USSR)

PRESENTED: January 27, 1958, by B. A. Kazanskiy, Member, Academy of Sciences, USSR

SUBMITTED: January 21, 1958

1. Esters-Synthesis
2. Carboxylic acids--Applications
3. Sulfuric acid catalysts--Applications

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5(

SOV/26-59-5-6/47

AUTHOR: Eydus, Ya.T., Doctor of Chemical Sciences

TITLE: Catalysis in the Production of Solid Polymers from Olefins.

PERIODICAL: Priroda, 1959, Nr 5, pp 35 - 40 (USSR)

ABSTRACT: The author stresses the importance of the catalytic method in modern chemical production, especially in the plastics industry, in which organic syntheses have been developed by G.G. Gustavson, I.L. Kondakov, S.V. Lebedev, N.D. Zelinskiy, L.G. Gurvich, S.S. Nametkin, V.N. Ipat'yev and others. Lately, the chief object of the polymerization of lower olefins was the production of high-quality lubricants. The author then describes ethylene polymerization at a pressure of 1,500 atmospheres and at a temperature of 190 - 210°C. The high pressure was later substituted by a process of polymerization of ethylene with the use of aluminum-organic compounds. One of the drawbacks

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5(3)

AUTHORS:

Puzitskiy, K. V., Eydus, Ya. T., Khudyakov, Yu. T.

TITLE:

On the Development of the Reaction of the Hydrogen-condensation of Carbon Monoxide With Ethylene Under a Pressure of 10 at  
(O protekanii reaktsii gidrokondensatsii okisi ugleroda s etilenom pod davleniyem 10 atm)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 5, pp 945 - 947 (USSR)

ABSTRACT:

The hydrogen-condensation of carbon monoxide with ethylene mentioned in the title has hitherto been investigated only under atmospheric pressure. In this case it was carried out at a pressure of 10 at. A metal velocity modulation tube was used as reactor in this investigation, which was built into a catalyzing furnace with automatic temperature control. The usual cobalt-clay (1:2) catalyst was used. The outflowing gas volume was rheometrically measured. The experiments were carried out at 190°. All other investigation conditions differed in no way from those of references 1,2. For comparison, the investigations were carried out also under atmospheric pressure. The following was determined: the yield of heavy (H) and light (L) olefins in ml/mm<sup>3</sup> H+L and H+L+G (G= gaseous olefins) at various mixing

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On the Development of the Reaction of the Hydrogen- SOV/62-59-5-36/40  
condensation of Carbon Monoxide With Ethylene Under a Pressure of 10 at

ratios  $\text{CO} + \text{C}_2\text{H}_4:\text{H}$ . CO was varied from 0.3-6.9%,  $\text{C}_2\text{H}_4:\text{H} \sim 3$ .  
The throughput was 100 hours<sup>-1</sup>. From the data obtained  
(Tables 1-2) it was found that the total olefin yield is only half  
of that obtained under atmospheric pressure. P=1 at: H+L=  
=290 ml/mm<sup>3</sup>, H+G+L= 525 ml/mm<sup>3</sup>. P= 10 at: H+L= 190 ml/mm<sup>3</sup> H+L+G=  
= 250 ml/mm<sup>3</sup>. With an increase of the carbon monoxide content  
from 0.3 to 6.4% the yield of heavy olefins compared to light  
olefins increased, while the gaseous ones decreased considerably.  
The total yield increased. The same development was found also  
in the case of experiments carried out at pressures of less  
than 10 at. Herefrom the authors drew the conclusion that with  
increasing CO-content in the initial mixture the degree of poly-  
merization of the obtained product increases. There are 2 tables  
and 5 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk  
SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of  
the Academy of Sciences, USSR)

SUBMITTED: November 12, 1958  
Card 2/2

5(3)

AUTHORS:

Eydus, Ya.T., Yershov, N.I.

SOV/62-59-7-23/38

TITLE:

On the Catalytic Hydrocondensation of Carbon Monoxide With Olefines (O kataliticheskoy gidrokondensatsii okisi ugleroda s olefinami).  
XX. The Relation of 3-Methyl-Butene-1 to the Catalysis of Hydrocondensation (Soobshcheniye 20. Otnosheniye 3-metilbutena-1 k gidrokondensatsionnuyu katalizu)

PERIODICAL:

Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1959, Nr 7, pp 1312 - 1317 (USSR)

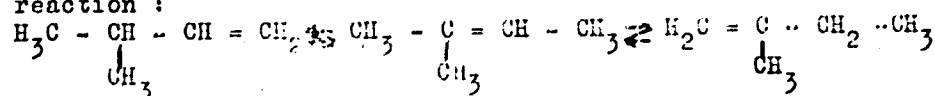
ABSTRACT:

Following a preceding paper, the present article investigates the polycondensation of isopropyl-ethylene or 3-methyl-butene-1 in the presence of carbon monoxide. In the experimental part, the synthesis of 3-methyl-butene-1 is first described, as an initial product usual isoamyl alcohol was applied. The Raman spectrum from the obtained 3-methyl-butene-1 was recorded and applied for analysis by means of a cyclohexane scale. The apparatus used and the catalyst for the polycondensation are described in a preceding paper (Ref 1). The experiments were carried out in a continuously working apparatus at

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On the Catalytic Hydrocondensation of Carbon Monoxide SOV/62-59-7-23/38  
With Olefines. XX. The Relation of 3-Methyl-Butene-1 to the Catalysis  
of Hydrocondensation.

atmospheric pressure and a temperature of 190°. The yield  
of hydropolymerisate, which was obtained, was 500 ml/m<sup>3</sup>.  
The condensation of 3-methyl-butene-1 was investigated  
under normal conditions in the presence of carbon monoxide  
or in the presence of carbon monoxide and molecular  
hydrogen. The results are summarized in table 1. The  
constants of the two fractions are obtained listed in table 2.  
In the fractions 2-methyl-butane-1 and 2 methyl-butene-1  
was obtained beside 10 - 11 % hydropolymerisate and  
hydrocondensate. In a stream of hydrogen the yield became  
greater. 58 % were hydrogenated and 3 % were isomerized.  
In the presence of carbon monoxide and molecular hydrogen  
12 % of isomeres with a displaced double bond could be  
obtained in the steam of the initial olefines, which arise  
on the surface of contacts, represented in the following  
reaction :



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On the Catalytic Hydrocondensation of Carbon Monoxide SOV/62-59-7-23/38  
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of Hydrocondensation

The data are given in Tables 3-5. Five fractions were obtained. From the last fraction the Raman spectrum was registered and the substances were identified. Finally, the authors thank V.T. Aleksanyan and Kh.Ye. Sterin of the Laboratory of the Committee of Spectroscopy of the Academy of Sciences, USSR for carrying-out the measurement of Raman spectrum. There are 2 figures, 6 tables, and 5 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N.D. Zelinskogo Akademii  
nauk SSSR  
(Institute of Organic Chemistry imeni N.D. Zelinskiy of the  
Academy of Sciences, USSR)

SUBMITTED: November 1, 1957

Card 3/3

5(3)  
AUTHORS: Puzitskiy, K.V., Terent'yeva, Ye.M., SOV/62-59-7-24/38  
Eydus, Ya.T.

TITLE: On the Catalytic Hydrocondensation of Carbon Monoxide With Olefines (O kataliticheskoy gidrokondensatsii okisi ugleroda s olefinami) XXI. Relations of Some Hydrocarbons With Conjugated Double Bonds to the Reaction of Hydrocondensation With Carbon Monoxide. (Soobshcheniye 21. Otnosheniye nekotorykh uglevodorodov s sopryazhennymi dvoynymi svyazami k reaktsii gidrokondensatsii s okis'yu ugleroda)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 7, pp 1318 - 1323 (USSR)

ABSTRACT: The reaction mentioned in the title has hitherto been applied to monoolefines of the acyclic and alicyclic lines (Refs 1-3). In this paper the attempt is made to extend the reaction also to di-olefines with conjugated double bonds. The apparatus used is described in references 1-2. The initial products were technical butadiene-1,3 and cyclopentadiene-1,3. The conditions for the reaction were

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On the Catalytic Hydrocondensation of Carbon Monoxide SOV/62-59-7-24/38  
With Olefines. XXI. Relations of Some Hydrocarbons With Conjugated Double  
Bonds to the Reaction of Hydrocondensation With Carbon Monoxide

atmospheric pressure and a temperature of  $190^{\circ}$ . The activity of the contacts and the yield of hydropolymerisates were great:  $500 - 600 \text{ ml/m}^3$  were obtained referred to  $(\text{CO}_2 + \text{H}_2 + \text{C}_2\text{H}_4)$ . The results of the experiments with butadiene-1,3 are listed in tables 1-2. From the data is evident that at the beginning, the reaction takes a slow course. Also the condenser was consumed very rapidly by the reaction of hydrocondensation. In the presence of an amount of hydrogen, which was enough to condense the entire butadiene and which was mixed with propylene, the reaction developed quite well. In the hydrocondensation with cyclopentadiene a small amount (4 - 5 %) of its mono-, di- and tri-derivates was formed, so that the cyclo-pentadiene as well as the hydrogenized cyclopentene were methylated. The cyclopentadiene dimerized in an amount of 20 %. The results of the analysis of the single fractions are given in other tables. The figures show the curves of distillation of the

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On the Catalytic Hydrocondensation of Carbon Monoxide SOV/62-59-7-24/38  
With Olefines. XXI. Relations of Some Hydrocarbons With Conjugated Double  
Bonds to the Reaction of Hydrocondensation With Carbon Monoxide

single fractions. There are 3 figures, 6 tables, and  
8 references, 7 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N.D. Zelinskogo Akademii  
nauk SSSR  
(Institute of Organic Chemistry imeni N.D. Zelinskiy of the  
Academy of Sciences, USSR)

SUBMITTED: November 15, 1957

Card 3/3

SOV/62-59-8-19/42

5(3), 5(4)  
AUTHORS:

Eydus, Ya. T., Ordyan, M. B.

TITLE:

On the Catalytic Hydrocondensation of Carbon Monoxide With Olefins. Communication 22. On the Problem of the Hydrocondensation of Carbon Monoxide with Cyclopentene

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 8, pp 1458-1464 (USSR)

ABSTRACT:

The present paper deals with the problem of the formation of hexacyclic ring hydrocarbons. First of all the question is asked whether rings can be obtained by means of an isomerization reaction of enlarged pentacyclic rings on hydrocondensation catalysts under analogous conditions. Tests were carried out with 1-methyl-cyclopentene-1 in a  $N_2$  and  $H_2$  flow over a contact, and with methylcyclopentane in a  $H$  current in a mixture of  $CO$  and  $H_2$ . Furthermore, the possibility of hydrogenolysis and hydrocracking of the said hydrocarbons was investigated. Tests were carried out with cyclopentane and hydrogen and by way of comparison with n-pentane and hydrogen. Catalyst, apparatus, and experimental procedure have already been described in references 1-3. All tests were carried out

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SOV/62-59-B-19/42

On the Catalytic Hydrocondensation of Carbon Monoxide With Olefins.  
Communication 22. On the Problem of the Hydrocondensation of Carbon  
Monoxide With Cyclopentene

at 190° and atmospheric pressure. The substances obtained from the reaction of 1-methylcyclopentene in a hydrogen current were identified and investigated by means of Raman spectra. The spectra were taken at the Commission of Spectroscopy of the Academy of Sciences, USSR by V. T. Aleksanyan and Kh. Ye. Sterin. Analyses of the gases obtained from the reaction of cyclopentane in a hydrogen current were carried out by T. I. Muzikina by means of the chromatographic method. It could be seen from the results that the reaction with enlarged pentacyclic rings does not take place in the above mentioned cases under the condition of a hydrocondensation of CO with olefins. Hydrogenolysis and hydrocracking of 1-methylcyclopentene-1, methylcyclopentene, cyclopentene, and n-pentene gave some ideas regarding the formation mechanism of some hydrocondensation products of cyclopentene with CO. The hydrocondensation of CO with cyclopentene resulted in hexacyclic rings due to an enlargement of the pentacyclic ring with side chains. These side chains formed during the reaction by means of the carbon atom of the CO molecule. There are

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SOV/62-59-8-19/42  
On the Catalytic Hydrocondensation of Carbon Monoxide With Olefins.  
Communication 22. On the Problem of the Hydrocondensation of Carbon  
Monoxide With Cyclopentene

5 tables and 12 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii  
nauk SSSR  
(Institute of Organic Chemistry imeni N. D. Zelinskiy of  
the Academy of Sciences, USSR)

SUBMITTED: November 19, 1957

Card 3/3

5 (3)

AUTHORS:

Evdus, Ya. T., Yerzhov, N. I.,  
Guseva, I. V.

SOV/62-59-8-20/42

TITLE:

On the Catalytic Hydrocondensation of Carbon Monoxide With  
Olefines. Communication 23. On the Hydrocondensation of Carbon  
Monoxide With Ethylene on Fe- and Ni Catalysts

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,  
1959, Nr 8, pp 1465-1470 (USSR)

ABSTRACT:

In the present paper an investigation is made of the possibility  
of polymerizing and hydropolymerizing ethylene and of hydro-  
condensating it with carbon monoxide on Ni- and Fe-Cu contacts  
as well as of the synthesis of hydrocarbons from CO and H<sub>2</sub>. For  
the investigation the contacts Fe-Cu-ThO<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub> marschalite  
(100:25:2:2:125), described in reference 4, and Ni-Mn-Al<sub>2</sub>O<sub>3</sub>  
Kisatibi diatomite (100:20:10:100) (Ref 5), with minor changes,  
were used. Experiments on the Fe-contact were carried out at  
250°, on the Ni-contact at 180°. Table 3 gives the results of  
the polymerization of C<sub>2</sub>H<sub>4</sub> on the Fe-contact. This contact is  
active for the synthesis of hydrocarbons from CO and H<sub>2</sub> but

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On the Catalytic Hydrocondensation of Carbon Monoxide With Olefines. Communication 23. On the Hydrocondensation of Carbon Monoxide With Ethylene on Fe- and Ni Catalysts

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inactive for the polymerization of ethylene. It does not become active for polymerization even after the synthesis of hydrocarbons. Table 4 gives the results of the hydropolymerization on contact 2. The activity of the contact with regard to the said reaction is rather small. The hydrocarbon yield did not exceed 9 ml/m<sup>3</sup>. Parallel investigations of the hydrocondensation of Co with C<sub>2</sub>H<sub>4</sub> in the presence of H<sub>2</sub> and the simultaneous synthesis of hydrocarbons from Co and H<sub>2</sub> on two Fe catalysts resulted in a 50-60 ml/m<sup>3</sup> yield of liquid hydrocarbons. Table 7 (polymerization and hydropolymerization of C<sub>2</sub>H<sub>4</sub> on two Ni catalysts) shows that this reaction cannot take place on Ni catalysts. Tables 8 and 9 give the results of the hydrocondensation of Co with C<sub>2</sub>H<sub>4</sub> on 3 Ni catalysts. The hydrocarbon yield from Co and H<sub>2</sub> was 110 ml/m<sup>3</sup>. The yield from the triple mixture CO-H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> was only 7-25 ml/m<sup>3</sup>. After this reaction the catalyst activity with regard to the hydrocarbon synthesis was

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On the Catalytic Hydrocondensation of Carbon  
Monoxide With Olefines. Communication 23. On the Hydrocondensation of Carbon  
Monoxide With Ethylene on Fe- and Ni Catalysts

SOV/62-59-8-20/42

smaller. The reaction processes on the individual catalysts  
are explained. There are 9 tables and 5 references, 4 of which  
are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii  
nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy  
of the Academy of Sciences, USSR)

SUBMITTED: November 21, 1957

Card 3/3



5(3)

AUTHORS:

Eydus, Ya. T., Yershov, N. I.

SOV/62-59-9-21/40

TITLE:

On the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen on a Mixed Cobalt-Nickel Catalyst

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, pp 1646-1648 (USSR)

ABSTRACT:

In the present paper the precipitation contact  $\text{Co-Ni-Mn-ThO}_2\text{-Al}_2\text{O}_3$ -kieselguhr in the ratio 50:50:10:9:5:100 is for the first time used for the synthesis of liquid hydrocarbons from CO and  $\text{H}_2$ , and its mode of action investigated. The catalyst was prepared by precipitating the components from their nitrate solutions by precipitating with potassium carbonate. The investigation was carried out at 198°C. Apparatus, purification, analysis, and experimental arrangement are described in reference 5. The experimental results are given in the table. Two series of tests were made in which a series of various contacts was applied. (1). A gas mixture of 1 CO:1.67  $\text{H}_2$  was passed over the catalyst at a throughput rate of 96-114/hr. After a few hours the liquid hydrocarbons separated. As long as the catalyst was fully active,

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On the Synthesis of Liquid Hydrocarbons From Carbon  
Monoxide and Hydrogen on a Mixed Cobalt-Nickel Catalyst

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the yield amounted to 191.9 ml/m<sup>3</sup>. (2) Gas mixture 1 CO:2 H<sub>2</sub>.  
Maximum yield after some hours 169.1 ml/m<sup>3</sup>. In both experiments  
a large quantity of methane separated first. From this it is  
assumed, that the catalytic surface for the synthesis of liquid  
hydrocarbons is formed in the first stage, involving the  
formation of methane. In the course of the reaction the formation  
of methane decreases. There are 1 table and 5 references, 1 of  
which is Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk  
SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the  
Academy of Sciences, USSR)

SUBMITTED: November 21, 1957

Card 2/2

5(3)

AUTHORS:

Eydus, Ya. T., Yershov, N. I.

SOV/62-59-9-22/40

TITLE:

On the Catalytic Hydrocondensation of Carbon Monoxide With Olefins Communication 24. On the Hydrocondensation of Carbon Monoxide With Ethylene on Cobalt-Nickel and Other Mixed Cobalt Catalysts

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, pp 1649-1654 (USSR)

ABSTRACT:

As had been shown previously, Co-catalysts can be used to advantage in the hydrocondensation of CO with ethylene, Ni-catalysts, however, only for the hydrogenation of  $C_2H_4$  to  $C_2H_6$  in the presence of CO. In the present paper an attempt is made to apply a mixed catalyst composed of CO and Ni, as well as Co-Fe and Co-Cu catalysts in the above hydrocondensation in the presence of  $H_2$  - CO and in the presence of  $H_2$  only. The mixed Co-Ni catalyst contained Mn,  $ThO_2$ , and  $Al_2O_3$  in addition to the two main components. Apparatus, purification, method of gas analysis, and procedure do not differ from those applied in the investigations described in references 1, 2. Results of the various

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On the Catalytic Hydrocondensation of Carbon Monoxide SOV/62-59-9-22/40  
With Olefins Communication 24. On the Hydrocondensation of Carbon Monoxide With  
Ethylene on Cobalt-Nickel and Other Mixed Cobalt Catalysts

polymerization and hydrocondensation reactions described in detail in the experimental part of the paper are given in tables 1-5. From the data obtained, the following findings are stressed: As was to be expected, the hydrocondensation of CO + ethylene proceeded best on a pure Co catalyst in the presence of slight amounts of Co. The formation of hydrocarbons from CO and H<sub>2</sub> was also effected by Fe and Ni catalysts. Good yields were obtained in the formation of hydrocarbons from CO, H<sub>2</sub>, and ethylene on mixed catalysts. Thus, apart from depending on the initial concentration of the substances investigated, the type of catalytic reaction also depends on the properties of the catalyst. At various concentration ratios of the initial substances the basic materials CH<sub>3</sub> or CH<sub>2</sub> can be formed (as surface radicals), which may then influence the further reaction. According to their effect the catalysts may be divided into condensing and hydrogenating catalysts. Ni catalysts hydrogenate olefins to form paraffins,

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On the Catalytic Hydrocondensation of Carbon Monoxide SOV/62-59-9-22/40  
With Olefins Communication 24. On the Hydrocondensation of Carbon Monoxide With  
Ethylene on Cobalt-Nickel and Other Mixed Cobalt Catalysts

Co-Ni catalysts have an essentially condensing effect, but owing to their Ni content also a hydrogenating effect: Thus, hydrocarbons are formed from CO, H<sub>2</sub>, and olefins but if the CO concentration is low hydrocondensation ensues. Co-Fe and Co-Cu catalysts have a good hydrogenating effect only. There are 5 tables and 5 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk  
SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the  
Academy of Sciences, USSR)

SUBMITTED: December 12, 1957

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5(3)

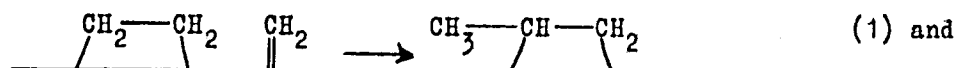
AUTHORS: Eydua, ~~Y. A. T.~~, Yerшов, N. I.

SOV/62-59-9-23/40

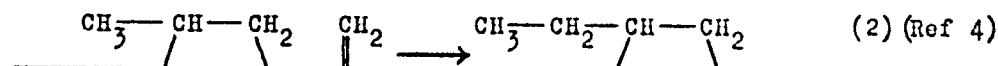
TITLE: On the Mechanism of Catalytic Hydropolymerization of Olefins Under the Action of Small Quantities of Carbon Monoxide in the Presence of Hydrogen

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, pp 1655-1662 (USSR)

ABSTRACT: In the present paper a detailed investigation is made on the strength of data given in publications as well as in papers by the authors concerning the mechanism of catalytic hydropolymerization of olefins in the presence of hydrogen under the action of small quantities of CO. It is known that  $\text{CH}_2$  radicals and olefins adsorbed to the catalyst interact in the presence of large quantities of CO to form the next higher homologs

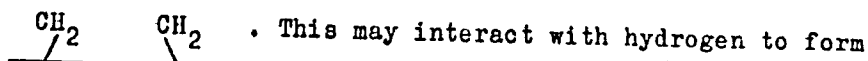
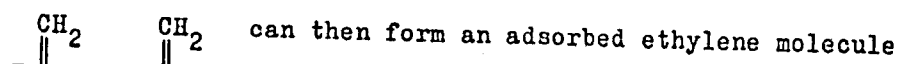
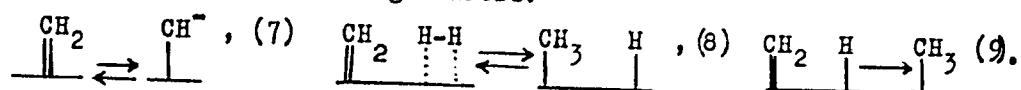
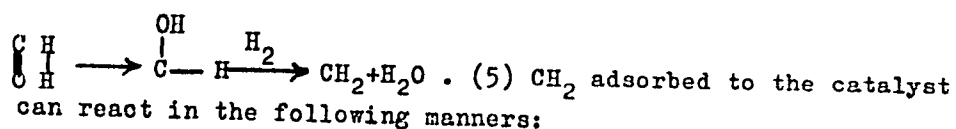


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On the Mechanism of Catalytic Hydropolymerization of Olefins Under the Action of Small Quantities of Carbon Monoxide in the Presence of Hydrogen SOV/62-59-9-23/40

A similar representation is given in reference 3: H is assumed to be adsorbed to the catalyst, initiating hydropolymerization by reacting with partially hydrogenated olefins. However, this representation does not give all the reaction processes involved. It must be assumed that the initiating centres consist of particles formed by



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On the Mechanism of Catalytic Hydropolymerization of Olefins Under the Action of Small Quantities of Carbon Monoxide in the Presence of Hydrogen SOV/62-59-9-23/40

paraffin radicals, or with other olefin radicals to yield alkyl radicals and atomic hydrogen. Olefin and atomic hydrogen also forms alkyl radicals. (13). This reaction was first described by Polanyi (Ref 18). Of the olefin radicals only  $\text{CH}_2$  is able to enter into reaction with the next higher homolog and give a higher homolog, other radicals do not react. Alkyl radicals, however, are much more reactive. They must be formed together with the adsorbed olefins by  $\text{CH}_2$  (formed by CO and H), and react with the olefin radicals, thus yielding higher alkyl radicals (15). The alkyl radicals themselves can give the following reactions: combining in pairs to give paraffin hydrocarbons, formation of paraffins with H, decomposition to adsorbed H and olefin (13). In the last reaction all possible isomers of this olefin may be formed, addition to an adsorbed olefin radical (15). Reaction with an  $\text{H}_2$  molecule and formation of a paraffin molecule.

Decomposition and formation of smaller alkyl radicals plus adsorbed olefins (19). This is especially the case with larger

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On the Mechanism of Catalytic Hydropolymerization of SOV/62-59-9-23/40  
Olefins Under the Action of Small Quantities of Carbon Monoxide in the Presence  
of Hydrogen

and less stable alkyl radicals. Both the reaction (15) and (19) are reversible. This is verified by the formation of olefins in hydropolymerization having a higher and lower number of carbon atoms. The mechanism of the catalytic hydropolymerization of olefins in the presence of hydrogen with small quantities of CO as initiator is based on the reactions (5), (8), (15), and (19). There are 27 references, 21 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk  
SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the  
Academy of Sciences, USSR)

SUBMITTED: November 21, 1957

Card 4/4

5.3400

77079

SOV/62-59-12-23/43

AUTHORS: ~~EYdus, Ya. T.~~, Gusyeva, I. V.

TITLE: Catalytic Polymerization of Olefins. Communication 2.  
Isomerization and Polymerization of Butene-1 Over  
Nickelous Oxide/Aluminum Silicate

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh  
nauk, 1959, Nr 12, pp 2195-2198 (USSR)

ABSTRACT: The catalytic activity of the catalyst NiO/aluminum  
silicate in regard to the migration of the double bond  
in butene-1 and its polymerization at atmospheric  
pressure, at 270° and a space velocity 1,400-1,600 hour<sup>-1</sup>,  
was studied. Attempts were made with three mixtures of  
butene-1 and butene-2 in ratios: 57.8:1; 1:1.1; and  
1:2.9. The yield of polymerization products was 8, 10,  
15% (whose nature was not described) and the yield of  
cracking products was 1, 2, 3%. The reaction does not  
take place in the absence of the above catalyst. The  
reaction over NiO/glass powder practically fails to take  
place (no isomerization; the yield of cracking products

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Catalytic Polymerization of Olefins. Communication 77079  
2. Isomerization and Polymerization of Butene-1 SOV/62-59-12-23/43  
Over Nickelous Oxide/Aluminum Silicate

was 3.3%). The results have shown that NiO has neither isomerizing nor polymerizing properties, and aluminum silicate must be considered to be active. There is 1 table; and 12 references, 7 Soviet, 5 U.S. The 5 U.S. references are: H. A. Cheney, S. H. Mc Allister, E. B. Fountain, J. Anderson, W. H. Peterson, Industr. and Engng. Chem. 42, 2580 (1950); J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, F. D. Rossini, J. Res. Nat Bur. Standards 36, No 6, 554 (1946); B. A. Lamb, E. E. Roper, J. Amer. Chem. Soc. 62, 806 (1940); C. D. Hurd, A. R. Goldsby, J. Amer. Chem. Soc. 56, 1812 (1934); H. H. Voge, G. M. Good, B. S. Greensfelder, Industr. and Engng. Chem. 38, 1033 (1946).

ASSOCIATION: Zelinskiy Institute of Organic Chemistry, Academy of Sciences, USSR (Institut organicheskoy khimii imeni N. D. Zelinskogo Akademii nauk SSSR)

SUBMITTED: March 26, 1958  
Card 2/2

5.3400

77083  
SOV/62-59-12-27/43

AUTHORS: Eydus, Ya. T., Puzitskiy, K. V., Guseva, I. V.

TITLE: Concerning the Catalytic Hydrocondensation of Carbon Monoxide With Olefins. Communication 25. The Influence of the Support on the Activity of Cobalt-Thorium Contact in the Hydrocondensation of Carbon Monoxide With Ethylene

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 12, pp 2213-2218 (USSR)

ABSTRACT: The above hydrocondensation was carried out in a flow system, with mixtures  $C_2H_4:H_2 = 1:0.8-1$ , containing 5-6% CO, at 190-200° and at atmospheric pressure. Space velocity was 100-120 hour<sup>-1</sup>. Regeneration was carried out with H<sub>2</sub>, at 450° for 3 hours. Catalysts were prepared by precipitation with K<sub>2</sub>CO<sub>3</sub> from their nitrate solutions, in the presence of the support. Prior to use, they were regenerated in a hydrogen atmosphere at 400-450°. For the Co/ThO<sub>2</sub> catalyst, silica gel, aluminum oxide,

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Concerning the Catalytic Hydrocondensation of Carbon Monoxide With Olefins. Communication 25. The Influence of the Support on the Activity of Cobalt-Thorium Contact in the Hydrocondensation of Carbon Monoxide With Ethylene

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SOV/62-59-12-27/43

activated charcoal, and muslyumovsk clay were used as support. Contact 1. Co/ThO<sub>2</sub>/silica gel (1:0.18:2) was inactive. Contact 2. Co/ThO<sub>2</sub>/silica gel (2:0.18:2) gave the average yield after 10 hours, 33.5 ml/1 · hour. Contact 3. Co/ThO<sub>2</sub>/activated charcoal (1:0.18:2) was slightly active. The catalytical activity of Co/ThO<sub>2</sub> decreases with replacement of silica gel by active charcoal. Contact 4 was similar to contact 3, giving the lower yield. Contact 5. Co/ThO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (1:0.18:5) was active. The yield was 43.3 ml/1 · hour. Ethylene reacted to the extent of 90-97%. 36-45% of it was converted into ethane. Several attempts (from 6 to 14) were made with muslyumovsk clay. It was found that the above clay (450°) can be an effective support for the contact Co/ThO<sub>2</sub>. Contact 15. Co/ThO<sub>2</sub>/muslyumovsk

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Concerning the Catalytic Hydrocondensation of Carbon Monoxide With Olefins. Communication 25. The Influence of the Support on the Activity of Cobalt-Thorium Contact in the Hydrocondensation of Carbon Monoxide With Ethylene

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clay-activated charcoal (1:0.18:2:1). The activity was smaller. Contact 16. Co/ThO<sub>2</sub>/muslyumovsk clay/Al<sub>2</sub>O<sub>3</sub> (1:0.18:2:1). The yield was 41.4 ml/l · hour. Contact 17. The ratio of the above components was 1:0.18:2:2. The yield was almost halved (17.7 ml/l · hour). Thus, the activity of Co/ThO<sub>2</sub> contacts, depending on support, decreases, as follows: muslyumovsk clay > diatomite > aluminum oxide > activated charcoal > silica gel. There are 5 tables; 1 figure; and 2 Soviet references.

ASSOCIATION: Zelinskiy Institute of Organic Chemistry, Academy of Sciences, USSR (Institut organicheskoy khimii imeni N. D. Zelinskogo Akademii nauk SSSR)

SUBMITTED: May 4, 1958  
Card 3/3

5(3)

AUTHORS:

Puzitskiy, K. V., Eydus, Ya. T., Ryabova, K. G., Guseva, I. V. SOV/79-29-9-45/76

TITLE:

On the Synthesis of Carboxylic Acid Derivatives From CO, Olefins, and Compounds Which May Be Acylated, in the Presence of Acid Catalysts. II. Syntheses of Isobutylene- and Butylene Esters

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 3019-3026 (USSR)

ABSTRACT:

In the present paper the experimental results concerning the carbalkoxylation of isobutylene and butylene are given. The first step of the synthesis of the esters was made according to Koch by reacting olefin with CO in the presence of concentrated  $H_2SO_4$ . Subsequently alcohol was added to the reaction mass instead of water. This led to good yields of esters of the carboxylic acids. The use of different alcohols led to different esters of the same acid. In experiments with only one alcohol a mixture of esters resulted with one or two esters predominating. The esters separated by rectification were identified among others according to the melting point of the

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On the Synthesis of Carboxylic Acid Derivatives From CO, Olefins, and Compounds Which May Be Acylated, in the Presence of Acid Catalysts. II. Syntheses of Isobutylene- and Butylene Esters

SOV/79-29-9-45/76

anilides obtained by the reaction with the esters with aniline magnesium bromide (Ref 5). The synthesis of the methyl- and ethyl esters from isobutylene and butylene, CO and methyl- and ethyl alcohol in the presence of sulphuric acid as catalyst takes place at increased pressure (80 atm) in higher yields than in normal case. The ester mixture obtained at increased pressure from isobutylene (about 65% yield, computed for the initial olefin and 100% for CO) contained esters of trimethyl acetic acid (53%),  $\alpha, \alpha$ -dimethyl butyric acid (6%), and  $\alpha, \alpha$ -dimethylvaleric acid (3-5%). In the ester mixture obtained from butylene under the same conditions (37-38% yield, computed for olefin and 81-89% for CO) esters of the  $\alpha$ -methyl butyric acid were obtained in yields from 53-60% and esters of trimethyl acetic acid in yields of 4%. The apparatus shown in figure 1 was used for the carboxylation of the olefins at atmospheric pressure. The conditions under which the experiments were carried out under pressure are shown in table 3. The curves and results of distillation of the ester mixtures are shown in figures 3, 4 and in tables 4-7. There are 4 figures, 7 tables, and 15 ref-

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SOV/79-29-9-45/76

On the Synthesis of Carboxylic Acid Derivatives From CO, Olefins, and Compounds Which May Be Acylated, in the Presence of Acid Catalysts. II. Syntheses of Isobutylene- and Butylene Esters

erences, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences USSR)

SUBMITTED: July 7, 1958

Card 3/3

S07/80-32-2-31/56

**AUTHORS:** Puzitskiy, K.V., Rabinovich, A.Ye., Eydus, Ya.T.

**TITLE:** The Synthesis of Detergents From Hydrocarbons of Synthol  
(Sintez moyushchikh veshchestv iz uglevodorodov sintina)

**PERIODICAL:** Zhurnal prikladnoy khimii, 1959, Vol XXXII, Nr 2,  
pp 404-408 (USSR)

**ABSTRACT:** The sodium salts of alkylbenzenesulfoacids which may be synthesized from petroleum fractions and artificial fuel are good detergents [Ref 1 - 5]. The synthesis of these detergents on the base of hydrocarbons from synthol is investigated here. In Table 2 the obtained monoalkylbenzenes are given. The physical constants of alkylates are a little increased due to the admixtures of diphenylalkanes formed during chlorination of the hydrated synthol. The aqueous solutions obtained from synthol fractions of C<sub>10</sub> - C<sub>15</sub> have good emulsifying properties. The samples obtained from the fractions C<sub>8</sub> - C<sub>13</sub> are resistant to hard water. The fractions C<sub>9</sub> - C<sub>15</sub> have a high foaming capacity. An increase of the pH raises the surface-active properties of the solutions: the surface tension and the wetting and emulsifying properties.

There are 5 tables and 5 references, 2 of which are Soviet, 2 English, and 1 American.

Card 1/2

The Synthesis of Detergents From Hydrocarbons of Synthol SOV/80-32-2-31/56

ASSOCIATION: Institut organicheskoy khimii imeni N.D. Zelinskogo AN SSSR; Mosk.  
filial Vsesoyuznogo nauchno-issledovatel'skogo instituta zhi-  
rov (Institute of Organic Chemistry imeni N.D. Zelinskiy of  
the USSR Academy of Sciences and the Moscow Branch of the All-  
Union Scientific Research Institute of Fats)

SUBMITTED: July 1, 1957

Card 2/2

SOV/80-32-2-34/56

AUTHORS: Eydus, Ya.T., Puzitskiy, K.V., Rabinovich, A.Yu.

TITLE: Synthesis of Detergents From Olefins Produced by Hydrocondensation of Carbon Monoxide With Ethylene and Propylene (Sintez moyushchikh veshchestv iz olefinov, poluchennykh gidrokondensatsiyey okisi ugleroda s etilenom i propilenom)

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Vol XXXII, Nr 2, pp 423-428 (USSR)

ABSTRACT: Sodium alkylbenzenesulfonates on the base of olefins prepared by catalytic hydrocondensation of carbon monoxide with ethylene and propylene are investigated here as to their surface-active and detergent properties. At low pH values aqueous solutions of alkylbenzene sulfonates show no emulsifying properties. The fractions of the ethylene hydrocondensate from C<sub>7</sub> to C<sub>11</sub> have a high resistance to hard and sea water. The foam of the fractions C<sub>12</sub> and C<sub>13</sub> is very abundant and dense. The detergent properties of alkylbenzenesulfonates of the fractions C<sub>10</sub> - C<sub>12</sub> are somewhat better than those of fat soaps. There are 5 tables and 3 references, 2 of which are Soviet and 1 American.

Card 1/2

SOV/80-32-2-34/56

Synthesis of Detergents From Olefins Produced by Hydrocondensation of Carbon Monoxide With Ethylene and Propylene

ASSOCIATION: Institut organicheskoy khimii imeni N.D. Zelinskogo i Moskovskiy filial VNII zhirov (Institute of Organic Chemistry imeni N.D. Zelinskiy and the Moscow Branch of the All-Union Scientific Research Institute of Fats)

SUBMITTED: July 1, 1957

Card 2/2

BYDUS, Ya.T., .doktor khim. nauk

Catalysis in the synthesis of solid polymers from olefins.

Prirada 48 no.5:35-40 My '59.

(MIRA 12:5)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR, Moskva.  
(Polymerisation) (Catalysis)

5(3)

AUTHORS:

Eydus, Ya. T., Nefedov, B. K.

SOV/20-124-1-31/69

TITLE:

Influence of Hydrogen Upon the Progress of Reaction of Iso-butylene Polymerization Over a Catalyst of Hydrocondensation of Carbon Monoxide With Olefins (O vliyanii vodoroda na protekaniye reaktsii polimerizatsii izobutilena nad katalizatorom gidro-kondensatsii okisi ugleroda s olefinami)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 1, pp 111 - 114 (USSR)

ABSTRACT:

If  $\alpha$ -olefins of normal structure, mixed with hydrogen, are conducted over the catalyst mentioned in the title (Co-loam), at 190° and atmospheric pressure, a small amount of liquid hydropolymerizate is formed in addition to the hydrogenation products of the olefin. Its yield increases with increasing molecular weight of the initial olefin (Ref 1). It was supposed that alkyl radicals form on the surface of the catalyst (semi-hydrogenated olefins) which are capable of initiating the hydropolymerization (Ref 5). Apparatus and experimental method are similar to those described in reference 6. Table 1 and figures 1 and 2 present the results. As can

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Influence of Hydrogen Upon the Progress of Reaction SOV/20-124-1-31/69  
 of Isobutylene Polymerization Over a Catalyst of Hydrocondensation of Carbon  
 Monoxide With Olefins

be seen from them, isobutylene could be polymerized up to 5% at the initial activity of the catalyst and up to 2% only at stabilized activity. The addition of 0.2%  $H_2$  increased the yield by the 2 - 2.5-fold. Between 0.2 and 10%  $H_2$  the yield remained unchanged, but with an increase in the  $H_2$ -concentration up to 50% increased again up to 18 and 12% at the initial and stabilized activity, respectively. At  $H_2$ -concentration above 50% the yield rapidly decreased. Together with the hydrogenation also hydro-cracking occurred. It was proved that n-butylenes could not be polymerized on the said catalyst. The sudden increase in the yield of the polymerizate on the addition of 0.2-0.3%  $H_2$  can only be explained by the formation of isobutyl radicals on the surface of the catalyst. The effect of hydrogen was observed only in the case of the Co-catalyst. The carrier of this catalyst (loam) which proved to be a much more active catalyst of isobutylene than Co-loam revealed that in this case hydrogen exerts no influence in the above sense. It rather acts as a diluent. This may point

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Influence of Hydrogen Upon the Progress of Reaction SOV/20-124-1-31/69  
of Isobutylene Polymerization Over a Catalyst of Hydrocondensation of Carbon  
Monoxide With Olefins

to the fact that no surface radicals are formed on loam, so that polymerization takes place according to the ionic mechanism only, predominantly forming a dimer and a trimer. On the catalyst Co-loam the process apparently possesses a mixed character, i.e. it partly proceeds according to the ionic and partly to the radical mechanism. There are 4 figures, 1 table and 10 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

PRESENTED: September 22, 1958, by B. A. Kazanskiy, Academician

SUBMITTED: September 18, 1958

Card 3/3

5(3)

AUTHORS:

Eydus, Ya. P., Nefedov, B. K.

SOV/20-127-5-27/58

TITLE:

On the Catalytic Destructive Hydropolymerization of Isobutylene Hydrogen Mixtures

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 5, pp 1029-1032 (USSR)

ABSTRACT:

The authors proved already earlier (Ref 1) that isobutylene, in contrast to the n-butylenes, may be polymerized at 190° and under atmospheric pressure in the presence of Co-clay (cobalt clay, catalyst of the hydrocondensation of carbon oxide with olefins), however, only to a small degree: 2 - 5 % yield in liquid polymerizate computed with respect to the olefin passed. An addition of hydrogen, however, brings about a rapid increase in the yield: by the double at 0.2 % H<sub>2</sub>, at the maximum up to 12 - 18 % in the case of an equimolar isobutylene hydrogen mixture. In the presence of clay this effect of hydrogen was not observed. In this reaction clay showed to be more active than the Co-clay catalyst. In the present paper the action of the hydrogen concentration on the polymerization and the hydropolymerization of isobutylene was to be investigated quantitatively and qualitatively. The authors

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. On the Catalytic Destructive Hydropolymerization of Isobutylene Hydrogen Mixtures SOV/20-127-5-27/58

wanted to find whether the reaction direction changes under the formation of products which do not only differ by the degree of saturation but also by the structure of the carbon skeleton. For this purpose the reaction products of isobutylene hydrogen mixtures were compared at different ratios of components. Tables 1 and 2 show the fractions obtained from the hydropolymerizate. The fractionation curves of these polymerizates are shown by figure 1. It may be seen from the results that under the given experimental conditions the direction of the reaction mentioned in the title depends on the hydrogen concentration in the initial mixture. In this connection two extreme directions may be distinguished:  
(1) Predominant formation of di- and triisobutylenes and their hydrogenated derivatives if no hydrogen or only small concentrations are present. (2) Formation of methyl alkanes and alkenes. Their methyl group is mainly in the 2nd carbon atom. This reaction takes place at a content of 50 % hydrogen in the initial mixture. In the case of intermediate concentrations both polymerization reactions take place. The first reaction has ionic character whereas the latter, strictly speaking, is

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On the Catalytic Destructive Hydropolymerization of  
Isobutylene Hydrogen Mixtures

SOV/20-127-5-27/58

no polymerization or hydropolymerization since its various stages are considerably influenced by processes of destructive hydrogenation. It must therefore be regarded as a destructive hydropolymerization of isobutylene under the action of hydrogen. Its mechanism will be further investigated. There are 1 figure, 2 tables, and 5 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

PRESENTED: April 22, 1959, by B. A. Kazanskiy, Academician

SUBMITTED: April 20, 1959

Card 3/3

5(3)

SOV/20-128-3-33/58

AUTHORS: Puzitskiy, K. V., Eydus, Ya. T., Ryabova, K. G., Guseva, I.V.

TITLE: Synthesis of Carboxylic Esters From Carbon Monoxide, Cyclo-olefines and Alcohols

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 3, pp 555-557 (USSR)

ABSTRACT: The authors reported on the synthesis method mentioned in the title and developed by them (Ref 1). The synthesis proceeds in 2 stages. Concentrated sulphuric acid was used as a catalyst. It was proved (Ref 2) that  $\alpha$ -olefines  $C_5-C_7$  of a normal structure in this reaction yield the ester of alkane acid which has by 1 carbon atom more than the initial olefine, and contains 2 methyl radicals in the molecule in  $\alpha$ -position. In most cases, an ester of the isomeric acid with one ethyl radical in  $\alpha$ -position originates in a smaller, but still considerable yield. In the 1st stage of synthesis, acyl-sulphuric acids (mixed sulphuric- and carboxylic-acid anhydrides) are temporarily formed which, in the 2nd stage, acylate the alcohols added. The present paper presents the results of the carbomethoxylation and carboethoxylation of cyclopentane and cyclohexene. Table 1 shows the ester synthesis from cyclo-olefines  $C_5-C_6$ . Table 2 shows the constants of the esters

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Synthesis of Carboxylic Esters From Carbon Monoxide, Cycloolefines and Alcohols

SOV/20-128-3-33/58

produced. Figures 1 and 2 present the distillation curves of these esters. There are 2 figures, 2 tables, and 12 references, 7 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR  
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

PRESENTED: June 3, 1959, by B. A. Kazanskiy, Academician

SUBMITTED: May 27, 1959

Card 2/2

[illegible]

reports to be presented at the 2nd Intl Congress on Catalysis, Paris, France, 4-9-Jul '60.

EYDUS, Ya. T.

"A Discussion of the Catalytic Reactions in the Hydro-polymerization  
of olefins and their hydro-condensation with carbon monoxide"

report presented at the General Conference of the Division of Chemical  
Sciences of the Academy of Sciences, USSR, 27-28 October 1960

So: Izvestiya Akademii nauk SSSR, otdeleniye khimicheskikh nauk, No. 2  
1961, Moscow, Pages 378-380



Abstracts and Index. Tenth Anniversary Issue  
 Problem Meeting 1 Session. [3] 20. Fifth 1. Physico-Chemical Institute  
 (Problems of Catalysis and Catalysis). [vol.] 20. Physics and Physico-  
 Chemistry of Catalysis) Moscow, Izdat. AN SSSR, 1960. 441 p. Extra  
 115 printed. 2,600 copies printed.

Vol. 1. G. E. Bogdanov, Corresponding Member of the Academy of Sciences USSR,  
 and O. V. Kravtsov, Candidate of Chemistry B. of Publishing House: A.L.  
 Khimicheskii Press. Msk. 64. 640 pages.

ABSTRACT: This collection of articles is addressed to physicists and chemists  
 and to the community of scientists in general interested in recent  
 research on the physics and physical chemistry of catalysis.

CONTENTS: The articles in this collection were read at the conference on the  
 Physics and Physical Chemistry of Catalysis organized by the Central Scientific  
 Secret AN SSSR (Committee of Chemical Sciences, Academy of Sciences USSR) and by  
 the Academic Council on the Problem of "the scientific bases for the selection  
 of catalysis". The Conference was held at the Tenth Anniversary khimskii  
 AN SSSR (Institute of Physical Chemistry of the AN SSSR) in Moscow March 20-23, 1960  
 or the great volume of material presented at the conference. Only papers not  
 published elsewhere were included in this collection.

## V. METHODS OF STRUCTURAL AND HEAT CONDUCTIVITY IN CRYSTALLINE

**Baldwin, A.L.**, [Treatises of Organic Chemistry of the AS EDS]. Structural and Stereochemistry of the Elementary Stages of Catalysts  
938

**Baldwin, A.L., and P. Tyrrel**. The Role of  $\alpha$ -Hydrogens in Catalysis; Reaction of Dehydrochlorination of Allyl Alcohol in the presence of Copper, Cobalt, Nickel, Iron, Silver, Platinum and Palladium  
939

**Dewar, R.H., and Baldwin, A.L.** [Treatises of Organic Chemistry of the AS EDS]. Bond Energy of Ethyl, Propyl, Butyl and Allylic Catalysts With the Elements of Organic Compounds  
940

**Thompson, V.J., and Baldwin, A.L.** [Treatises of Organic Chemistry of the AS EDS]. Oxidation Cycle Catalysts as Benzene Bond Energy by the Electric Method With a View to Sorting Out a Theory for the Selection of Catalysts  
951

**Vanderhoff, V.J., and Baldwin, A.L.** [Treatises of Organic Chemistry of the AS EDS]. Investigation of the Elementary Stages of the Alcohol Degradation Reaction Over Al<sub>2</sub>O<sub>3</sub> Catalysts  
956

**Baldwin, A.L., and F.P. Boehm**. [Treatises Of Organic Chemistry of the AS EDS]. Catalytic Properties of Solid-Supporter known as Specific Differences  
963

**T. BENTLEY AND CALVIN CONTRIBUTIONS IN CATALYSIS**

**Irradiability, V.V.** [Treatises of Chemical Physics of the AS EDS]. Data Contributions to heterogeneous Catalysis:  
969

**Fremy-Aldges** [Oxide of Inorganic Chemistry of the A. Hochstein University Press]. Structure of Heterogeneous Catalysts and the Mechanism of Certain Catalytic Reactions  
970

**Hinkle, R.D., and L.O. Pryor**[Organometallic Inertness Level A.Ta. Paper] Using a Self-Heating Apparatus to Study the Chain Characteristic of Surface Reactions  
990

**Loomis, J.B., and Irradiability, V.V.** [Treatises of Chemical Physics of the AS EDS]. On the Problem of the Possibility of Chain Mechanisms During Catalysts Over Metals  
996

**Rosen, M.S., and F.P. Tyner** [Treatises of Organic Chemistry Level A.Ta. Aldrich & Co.] Role of Free Radicals in the Mechanism of Hydrogen-oxidation of Chlorine Under the Action of Small Quantities of Carbon Monoxide in the Presence of Endoxone  
998

ZELINSKIY, Nikolay Dmitriyevich, akademik [1861-1953]; KAVERZNEVA,  
Ye.D., doktor khim.nauk, otv.red.; PLATE, A.F., doktor khim.nauk,  
red.; RUBINSHTEYN, A.M., doktor khim.nauk, red.; BYDUS, Ye.T.,  
doktor khim.nauk, red.; BRUSOV, I.I., red.izd-va; TIKHOMIROVA,  
S.G., tekhn.red.

[Collected works] Sobranie trudov. Moskva, Izd-vo Akad.nauk  
SSSR. Vol.4. 1960. 598 p. [\_\_\_Author and subject index]  
\_\_\_Imennoi i predmetnyi ukazateli. 26 p. (MIRA 14:2)  
(Zelinskii, Nikolai Dmitriyevich, 1861-1953)  
(Chemistry, Organic)

5 3300, 5 1190

SCY 00-00-1-20/37

AUTHORS: Eydus, Ya. T. , Pozitskiy, K. M., Yershov, N. I.,  
Kazanskiy, B. A.

TITLE: Catalytic Polymerization of Olefines. Communication  
III. Concerning the Activity of Nickel Monoxide-Silica  
Gel Catalyst in Ethylene Polymerization

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh  
nauk, 1960, Nr 1, pp 111-114 (USSR)

ABSTRACT: From 15 silica gel brands (ASM, ASK, KSK, ShSK, ShSM,  
MSM, KSM) only the brand KSK was found suitable for  
the preparation of active NiO-containing catalysts.  
KSK alone showed no catalytic properties with respect  
to ethylene polymerization. The activity of NiO-KSK  
catalysts prepared from various KSK samples was not  
uniform and showed wide variations. This could be  
explained by the presence of  $Al_2O_3$  impurities which  
imparted catalytic properties to silica gel. This  
will be discussed in future studies. There are 4

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Catalytic Polymerization of Chlorines.  
Communication III

78074  
SOV/62-60-1-20/37

tables; and 9 references, 3 U.S., 3 Japanese, 3 Soviet. The 3 U.S. references are: H. D. Foster, Industr. & Engng. Chem., 29, 1254 (1937); F. H. Gayer, ibid., 25, 1122 (1933); S. J. Hatzel, R. M. Kennedy, Chem. Abstr., 43, 1218, 5540 (1949).

ASSOCIATION:

N. D. Zelinskiy Institute of Organic Chemistry,  
Academy of Sciences USSR (Institut organicheskoy  
khimii imeni N. D. Zelinskogo Akademii nauk SSSR)

SUBMITTED:

May 4, 1958

Card 2/2

5.1150, 5.3300

78075  
SOV/62-60-1-21/37

AUTHORS: Ya. T. Eydus, Puzitskiy, K. V., Kazanskiy, B. A.

TITLE: Catalytic Polymerization of Olefines. Communication IV. Concerning the Polymerization of Ethylene Over Nickelous Oxide-Silica Gel Catalyst Promoted by Aluminum Oxide

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, Nr 1, pp 115-119 (USSR)

ABSTRACT: Continuing a previous study of silica gel-NiO catalysts (this journal, 1960, p 111, our abstract 78074), the authors investigated the polymerization of ethylene at 300° C under atmospheric pressure, using KSK silica gel-NiO catalysts with the addition of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in concentrations varying from 0.025 to 10.0%. The addition of the latter increased considerably the activity of the catalyst. The activity changed little in the aluminum nitrate concentration range 0.5-10% but decreased rapidly at concentrations below 0.5%. Only KSK silica gel,

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Catalytic Polymerization of Olefines.  
Communication IV

78075  
SOV/62-60-1-21/37

as carrier of aluminum oxide, and nickelous oxide gave positive catalytic results. Catalysts prepared from NiO on other carriers, such as aluminum oxide, kieselguhr, various clays, or activated carbons were inactive. Catalyst NiO-Al<sub>2</sub>O<sub>3</sub>-KSK prepared from nickelous nitrate by precipitation with potassium carbonate were inactive. Catalyst obtained by precipitation with aqueous ammonia solution was active but insufficiently stable. Its regenerative capacity, as well as selectivity with respect to dimerization of ethylene was somewhat increased by addition of zinc oxide. There are 3 tables; 1 figure; and 6 references, 3 U.S., 1 U.K., 2 Soviet. The 4 U.S. and U.K. references are: S. J. Hetzel, R. M. Kennedy, U.S. Pat. 2452190 (1948); Phillips Petr. Co., Brit. Pat. 619231 (1949); J. P. Hogan, R. L. Banks, W. C. Lanning, A. Clark, Industr. & Engng. Chem., 47, 752 (1955); H. A. Cheney, S. H. McAllister, E. B. Fountain, J. Anderson, W. H. Peterson, *ibid.*, 42, 2580 (1950).

Card 2/3

Catalytic Polymerization of Olefines  
Communication IV

78075  
SOV/62-60-1-21/37

ASSOCIATION: N. D. Zelinskiy Institute of Organic Chemistry,  
Academy of Sciences USSR (Institut organicheskoy  
khimii imeni N. D. Zelinskogo Akademii nauk SSSR).

SUBMITTED: May 21, 1958

Card 3/3

5.1190, 5.3300

78076  
SOV/62-60-1-22/37

AUTHORS: Eydus, Ya. T., Yershov, N. I.

TITLE: Concerning the Catalytic Hydrocondensation of Carbon Monoxide with Olefins. Communication XXVI. The Effect of the Addition of Metal Oxides on the Activity of Cobalt-Kieselguhr (Kisatibi) Catalyst in Hydrocondensation of Carbon Monoxide with Ethylene and Hydropolymerization of the Latter with Carbon Monoxide

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960. Nr 1, pp 120-124 (USSR)

ABSTRACT: The condensation of  $C_2H_4 + H_2$  (1:0.8) mixtures containing 5-6% CO over cobalt-kieselguhr catalyst with and without addition of various condensation-promoting agents was investigated. The reaction of pure Co-kieselguhr catalyst proceeded chiefly in the direction of the hydrogenation of ethylene to ethane (up to 70%, based on reacted ethylene). The addition of MgO to the catalyst practically did not change the direction of the reaction.

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Concerning the Catalytic Hydrocondensation of  
Carbon Monoxide with Olefins. Communication  
XXVI

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SOV/62-60-1-22/37

The simultaneous addition of  $MnO$  and  $Al_2O_3$  reduced the activity and the stability of the catalyst. The addition of  $V_2O_5$  (Co- $V_2O_5$ -kieselguhr in 1:0.02-0.06:1 ratio) increased the condensing properties and lowered the hydrogenating properties of the catalyst as was evidenced by the reduced relative yield of the  $C_3 + C_4$  fraction, and the reduced yield of ethane. There are: 4 tables; and 5 references, 1 U.S., 4 Soviet. The U.S. reference is: C. H. Riesz, F. Lister, L. G. Smith, V. I. Komarevsky, Industr. & Engng. Chem., 40, 718 (1948).

ASSOCIATION: N. D. Zelinskiy Institute of Organic Chemistry, Academy of Sciences USSR (Institut organicheskoy khimii imeni N. D. Zelinskogo Akademii nauk SSSR)

SUBMITTED: May 21, 1958

Card 2/2

5.3300

18577  
304/02-0041-23/37

AUTHORS: Eydas, Ya. T., Nefyedov, B. K.

TITLE: Brief Communications. Concerning Conversions of Diisobutylene (2,4,4-Trimethyl-1-pentene) Under the Conditions of Destructive Hydropolymerization of Isobutylene

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, Nr 1, pp 125-127 (USSR)

ABSTRACT: It was shown previously (Ya. T. Eydas, B. K. Nefyedov, Dok. AN SSSR, 124, 111, 1959; and Ya. T. Eydas, B. K. Nefyedov, Dok. AN SSSR, 127, 1029, 1959) that an equimolar mixture of isobutylene and hydrogen undergoes a specific conversion over the Co-city catalyst at 190°C at atmospheric pressure; the destructive hydropolymerization of isobutylene. There are three possible routes: the actual polymerization of isobutylene with formation of diisobutylene and products of its hydrogenation, which subsequently undergo hydrocracking and disproportionation; and reaction between the alkyl radicals (formed

Card 1/6

Brief Communications. Concerning Conversions  
of Diisobutylene (2,4,4-Trimethyl-1-pentene)  
Under the Conditions of Destructive Hydro-  
polymerization of Isobutylene

76077

SOV/62-60-1-23/37

by the hydrocracking of isobutylene dimers and trimers) and the initial isobutylene; and hydrocracking of isobutylene with formation of methyl and other radicals which react with the molecules of isobutylene adsorbed on the catalyst's surface. Experiments were conducted in order to find which of these processes takes place. The procedure and apparatus used were described previously (see above references). A mixture of diisobutylene and hydrogen in different proportions (from 1.8 to 13.9) was passed through a glass tube (10 mm in diameter) filled with Co-clay catalyst, under atmospheric pressure, at 190°. Duration of the individual experiments was 10-20 hours. The results are shown in the Table and in Figs. 1 and 2. It was shown that under the above conditions, hydrogenation of 2,4,4-trimethyl-1-pentene 2,4,4-trimethylpentane takes place. The isomerization of the carbon skeleton, hydrocracking, and molecular disproportionation in a wide range of  $H_2/C_5H_{10}$  take

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78077, SOV/62-60-1-23/37

Key to Table: (a) Experiment Nr; (b) Molar ratio of  $H_2:C_8H_{16}$  in the initial vapor-gas mixture; (c) Summary space velocity of the initial vapor-gas mixture; (d) Yield of the product of catalysis, % by volume, based on the initial  $C_8H_{16}$ ; (e) Content of unsaturated products in the product of catalysis, in %; (f) Yield of the hydrocracking products  $C_5-C_7$  in the products of catalysis; (\*) in this experiment, beside  $H_2$  and  $C_8H_{16}$ , isobutylene, in proportion  $H_2:C_4H_8 = 1$ , also passed through.

a	b	c	d	e	f
1	1,8	116	100	14	15,4
2	8,7	109	89,7	1,5	18,7
3	10,7	184	95	0,0	20,8
4	13,9	172	96,0	0,0	17,5
5	1,2*	93	101,7	72,4	9,0

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73077, SOV/62-50-1-23/37

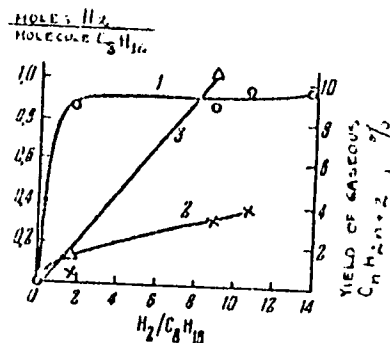


Fig. 1. Relationship between the ratio  $H_2:C_8H_{16}$  and the quantity of  $H_2$  (in moles per mole of the initial  $C_8H_{16}$ ) used for hydrogenation (curve 1), for hydrocracking (curve 2), and yield (in %, based on the initial  $C_8H_{16}$ ) of gaseous products of cracking (curve 3).

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70011, 50, 10-1-85/3

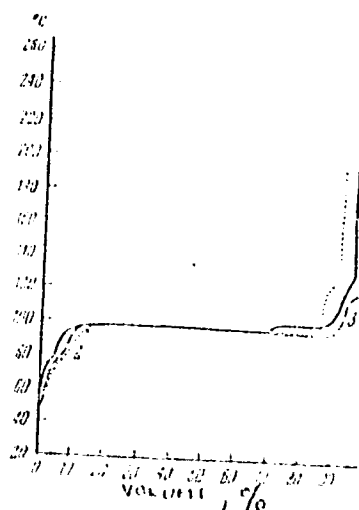


Fig. 2. Fractional distillation of the products of catalysts: (1) experiment 1; (2) experiment 2; (3) experiment 2; (3) experiment 3.

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Brief Communications. Concerning Conversions of Diisobutylene (2,4,4-Trimethyl-1-pentene) Under the Conditions of Destructive Hydro-polymerization of Isobutylene 78077  
SOV/62-60-1-23/37

place only to a small extent. It was suggested that the formation of 2-methyl substituted hydrocarbons in the products of destructive hydropolymerization of isobutylene is a result of the hydrocracking of isobutylene and the reaction between the products of cracking (alkyl free radicals) and the molecules of isobutylene adsorbed on the catalyst. There is 1 table; 2 figures; and 5 Soviet references.

ASSOCIATION: N. D. Zelinskiy Institute of Organic Chemistry, Academy of Sciences, USSR (Institut organicheskoy khimii imeni N. D. Zelinskogo Akademii nauk SSSR)

SUBMITTED: April 27, 1959

Card 6/6

*Eydus, Ya. T.*

82045  
S/062/60/000/02/10/012  
B003/B066

53830A

AUTHORS: Eydus, Ya. T., Nefedov, B. K.

TITLE: Hydropolymerization of Isobutylene<sup>1</sup> on Cobalt - Clay  
Catalyst<sup>1</sup> Under Simultaneous Action of Hydrogen and Carbon  
Monoxide

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,  
1960, No. 2, pp. 349 - 351

TEXT: The influence exercised by CO (in different concentrations) and H<sub>2</sub>  
(in different volume ratios to isobutylene) upon the hydropolymerization  
of isobutylene was investigated. The experiments were carried out on a  
Co - clay catalyst at atmospheric pressure and 190°C. The results ob-  
tained are illustrated in diagrams (Figs. 1, 2, 3). The maximum yield of  
liquid hydropolymerizate was obtained at a content of 2 - 4% Co in the  
initial mixture and an isobutylene - hydrogen mixture in a mixing ratio  
of i-C<sub>4</sub>H<sub>8</sub> : H<sub>2</sub> = 2 : 1. When using clay alone as catalyst, neither an  
influence of H<sub>2</sub> nor of Co upon the polymerization was found to occur. It

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Hydropolymerization of Isobutylene on  
Cobalt - Clay Catalyst Under Simultaneous  
Action of Hydrogen and Carbon Monoxide

02045  
S/062/60/000/02/10/012  
B003/B066

is assumed from the results obtained that the presence of a Co - clay catalyst effects a hydropolymerization according to the radical mechanism, whereas the reaction on the clay catalyst takes place by the ion mechanism. There are 3 figures, 1 table, and 5 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: June 1, 1959

Card 2/2

S/062/60/000/03/06/007  
B008/B006

AUTHORS: Eydus, Ya. T., Puzitskiy, K. V., Kazanskiy, B. A.

TITLE: Catalytic Polymerization of Olefines. 6. Effect of Some  
Metal Oxides on the Activity of NiO-Al<sub>2</sub>O<sub>3</sub>-Silica Gel (KSK)  
Catalyst in Polymerization of Ethylene

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh  
nauk, 1960, No. 3, pp. 513-518

TEXT: The effect of admixtures of copper, silver, zinc, magnesium, calcium, barium, thorium, and manganese oxides on the activity of a NiO-Al<sub>2</sub>O<sub>3</sub>-silica gel catalyst type KCK (KSK) was investigated. These admixtures were introduced by treating the boiling silica gel with aqueous solutions of the corresponding nitrate. For the rest, the methods and apparatus described in Refs. 1 and 2 were used. The results obtained are listed in Tables 1 and 2. For comparison, experimental data from experiments carried out using corresponding catalysts containing no metal oxide admixtures except Al<sub>2</sub>O<sub>3</sub> are shown in Table 3. It was found

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Catalytic Polymerization of Olefines. 6.  
Effect of Some Metal Oxides on the Activity  
of  $\text{NiO-Al}_2\text{O}_3$ -Silica Gel (KSK) Catalyst in  
Polymerization of Ethylene

S/062/60/000/03/06/007  
B008/B006

that the activity of the catalyst is strongly reduced by admixtures of silver-, calcium-, and barium oxides, and slightly by thorium dioxide. Admixtures of copper-, zinc-, manganese-, and magnesium oxides have hardly any effect. The selectivity of the catalyst with respect to ethylene dimerization is considerably increased by adding copper-, silver-, zinc-, barium-, and manganese oxides, and, to a lesser extent, by the addition of calcium- and magnesium oxides. The catalytic stability of the contact is strongly reduced by silver- and calcium oxide admixtures. Manganese oxide has the reverse effect. Regeneration of the catalyst is inhibited by the addition of copper- and zinc oxides, and is impossible if the catalyst contains silver-, magnesium-, calcium- and barium oxides. Catalysts mixed with silver-, magnesium-, and calcium oxides lose their selectivity when treated with air at  $450^\circ\text{C}$ . In catalysts containing magnesium oxide however, selectivity is preserved. Yu. A. Bitepazh is mentioned. There are 3 tables and 20 references, 16 of which are Soviet. ✓

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Catalytic Polymerization of Olefines. 6.  
Effect of Some Metal Oxides on the Activity  
of NiO-Al<sub>2</sub>O<sub>3</sub>-Silica Gel (KSK) Catalyst in  
Polymerization of Ethylene

S/062/60/000/03/06/007  
B008/B006

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo  
Akademii nauk SSSR (Institute of Organic Chemistry imeni  
N. D. Zelinskiy of the Academy of Sciences, USSR) ✓

SUBMITTED: July 21, 1958

Card 3/3

EYDUS, Ya.T.; YERSHOV, N.I.; PUZITSKIY, K.V.; GUSEVA, I.V.

Catalytic hydrocondensation of carbon monoxide with olefins.  
Report No.28: Activity of the cobalt - clay contact in the  
hydrocondensation of carbon monoxide with ethylene and polymeri-  
sation of the latter under the influence of carbon monoxide. Izv.  
AN SSSR Otd.khim.nauk no.5:913-919 My '60.

(MIRA 13:6)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii  
nauk SSSR.

(Carbon monoxide) (Ethylene) (Catalysts)

EYDUS, Ya.T.; PUZITSKIY, K.V.; KAZANSKIY, B.A.

Catalytic polymerization of olefins. Report No.9: Activity of a nickel silicate deposited on an aluminosilicate in the course of ethylene polymerization. Izv.AN SSSR Otd.khim.nauk no.5:926-930 My '60. (MIRA 13:6)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii nauk SSSR.

(Nickel silicate) (Ethylene) (Polymerization)

KYDUS, Ya.T.; PUZITSKIY, K.V.; YERSHOV, N.I.; KAZANSKIY, B.A.

Catalytic polymerisation of olefins. Report No.10: Effect of the temperature and contact time on the course of ethylene polymerisation on nickel catalysts. Izv.AN SSSR.Otd.khim. nauk no.6:1114-1118 J1 '60. (MIRA 13:7)

1. Institut organicheskoy khimii imeni M.D.Zelinskogo  
Akademii nauk SSSR.  
(Ethylene) (Polymerization) (Catalysts, Nickel)

S/062/60/000/007/015/017/XX  
B004/B064

AUTHORS: Eydus, Ya. T., Puzitskiy, K. V., Yershov, N. I.,  
Guseva, I. V., and Kazanskiy, B. A.

TITLE: Catalytic Polymerization of Olefins. Communication 11.  
The Effect of Impurities in the Initial Gas and of the  
Material of the Test Tube Wall Upon the Course of the  
Polymerization Reaction of Ethylene on Nickel Catalysts

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh  
nauk, 1960, No. 7, pp. 1291 - 1294

TEXT: The authors are concerned with studying the effects of all  
reaction conditions upon the catalytic polymerization of olefins. In  
the present paper, they report on the effect of impurities in initial  
ethylene, the influence exerted upon the catalyst by treating it with  
various substances, and finally the effect exerted upon catalysis  
by the material of the tube walls. Up to 5% propylene or up to 10%  
butylene were added to ethylene as impurities. Ethylene was polymerized

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Catalytic Polymerization of Olefins. S/062/60/000/007/015/017/XX  
 Communication 11. The Effect of Impuri- B004/B064  
 ties in the Initial Gas and of the  
 Material of the Test Tube Wall Upon the Course of the Polymerization  
 Reaction of Ethylene on Nickel Catalysts

to butylene on a  $\text{NiO-Al}_2\text{O}_3$  catalyst. While an addition of 0.5 to 3%  
 impurities showed no effect, the activity of the catalyst decreased at  
 higher amounts of admixtures (yield without addition: 82%, with an  
 addition of 5%: 56.2%). An addition of 30 - 40%  $\text{H}_2$  or preliminary  
 treatment of the catalyst with  $\text{H}_2$  (yield without  $\text{H}_2$ : 58.8%, with  $\text{H}_2$ :  
 23.0%) showed the same effect. The water vapor content of ethylene  
 also reduced the activity of the catalyst. On comparing the activity  
 of the catalyst in test tubes of glass, brass, or stainless steel it  
 was found that in the steel tube the yield in polymers and the regenera-  
 tion capacity of the catalyst decrease: maximum yield in the glass-  
 and brass tubes 71.2%, in the steel tube 64.7%. There are 1 figure,  
 5 tables, and 2 Soviet references.

Card 2/3

Catalytic Polymerization of Olefins. S/062/60/000/007/015/017/XX  
Communication 11. The Effect of B004/B064  
Impurities in the Initial Gas and of the  
Material of the Test Tube Wall Upon the Course of the Polymerization  
Reaction of Ethylene on Nickel Catalysts

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo  
Akademii nauk SSSR  
(Institute of Organic Chemistry imeni N. D. Zelinskiy  
of the Academy of Sciences USSR)

SUBMITTED: November 12, 1958

Card 3/3

EYDUS, Ya.T.; YERSHOV, N.I.

Role of flat chains in the mechanism governing the catalytic  
hydropolymerization of olefins under the influence of small  
amounts of carbon monoxide and in the presence of hydrogen.  
Probl. kin. i kat. 10:404-409 '60. (MIRA 14:5)

1. Institut organicheskoy khimii imeni N.D.Zelinskogo AN SSSR.  
(Polymerization) (Olefins) (Carbon monoxide)

S/062/60/000/011/010/016  
B013/B078

AUTHORS: Eydus, Ya. T., Nefedov, B. K.

TITLE: Catalytic Hydrocondensation of Carbon Monoxide With Olefins and Their Hydropolymerization Under the Action of Carbon Monoxide and Hydrogen. Report 29. The Behavior of 2,4,4-Trimethylpentene-1 Toward Hydrocondensation Catalysis

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 11, pp. 2037 - 2041

TEXT: The present paper deals with the behavior of isobutylene-2,4,4-trimethylpentene-1 toward the hydrocondensation of CO dimers. At first the behavior of an olefin was investigated, then its mixtures with hydrogen (Ref.5) and, finally, the ternary  $C_8H_{16}-H_2-CO$  mixtures. The experimental methods and apparatus differed in no way from those described in Refs. 1-5. The 2,4,4-trimethylpentene-1 used was synthesized by the method of A. M. Butlerov (Ref.6) via polymerization of isobutylene under

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